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Synthesis of a new ramsdellite-like phase of approximate composition, $Li_2MgSn_3O_8$

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The complex oxides $Li_2Ti_3O_7$ [1–4] and $LiFeSnO_4$ [5, 6] have crystal structures that are derived from ramsdellite, MnO_2 [7]. The ramsdellite structure contains MnO_6 octahedra which link together, by sharing edges, to form infinite double chains. These double chains link up, at their corners, with adjacent chains to form a three-dimensional framework. Between adjacent double chains lie empty tunnels which are capable of being occupied by Li^+ ions. In $Li_2Ti_3O_7$, the framework constitution may be written as $(Li_{0.5}Ti_3)O_7$, in which Li^+ and Ti^{4+} ions are distributed at random over the octahedral sites [4]. The remaining 1.5 Li^+ ions occupy sites in the tunnels. In $LiFeSnO_4$, the framework has the constitution $(Fe, Sn)O_4$, again with a random distribution of Fe^{3+} and Sn^{4+} ions, and all the Li^+ ions are located in the tunnels [5]. We have prepared a new phase, of composition close or equal to $Li_2MgSn_3O_8$, which is also ramsdellite-like. Its framework has the constitution $(Mg, Sn_3)O_8$ and Li^+ ions reside in the tunnels, although their precise location is not known.

The new phase was encountered during a study of compound formation in the system Li_2O–MgO–SnO_2. It was prepared by a solid state reaction, using Li_2CO_3, $Mg(NO_3)_26H_2O$ and SnO_2 in the molar ratio 1:1:3 as starting materials, in platinum crucibles in an electric muffle furnace. The temperature was raised slowly from 100 to 600° C, in order to expel gases, the mixture was left at 600° C for a few hours and then heated to 900° C for a few hours. The sample was then removed from the furnace and crucible, crushed and returned at ~1150° C for a few hours. The product, identified by X-ray powder diffraction (Philips, Hägg Guinier camera, Cu$K\alpha_1$ radiation), was essentially the new phase with a small amount of residual SnO_2.

TABLE I Unit cell dimensions of ramsdellite phases

	a (nm)	*b* (nm)	*c* (nm)
$Li_2Ti_3O_7$ [8]	0.954_5	0.294_5	0.501_5
$LiFeSnO_4$ [5]	0.9874	0.3066	0.5066
$Li_2MgSn_3O_8$*	1.000_7	0.3109_4	0.510_9

*Parameters determined by least squares refinement. KCl internal standard ($a = 0.62931$ nm) added to the sample.

The difficulty in deciding the exact composition of the new phase was that preparations in this system were prone to lithia loss, especially on heating above ~1000° C. An attempt was made, using analytical transmission electron microscopy, to determine the magnesium/tin ratio in small crystals but the results were of insufficient accuracy to pinpoint the composition. It was concluded that the composition is most probably $Li_2MgSn_3O_8$; less probably, it could be a non-stoichiometric phase with a few per cent extra lithia and perhaps a small deficiency of magnesia.

The new phase is thermodynamically stable only at high temperatures, $\gtrsim$1150° C, although it may be preserved readily at room temperature where it is kinetically stable. It is interesting that the other two ramsdellite phases, $Li_2Ti_3O_7$ and $LiFeSnO_4$, are also high temperature phases with a lower limit of stability [5, 8, 9].

From a comparison of the X-ray powder data of the new phase with those of $Li_2Ti_3O_7$ and $LiFeSnO_4$, it seemed very likely that the new phase also had a ramsdellite structure. This was confirmed by indexing the powder pattern on a similar orthorhombic unit cell, Table I, and calculating the X-ray line intensities for comparison with the experimental values. For the calculations, the atomic coordinates given in [5] for (Fe, Sn),

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TABLE II Atomic coordinates used for intensity calculations

Atom	x	y	z	B	Occupancy
Mg	0.1418	0.25	0.98	0.76	0.25
Sn	0.1418	0.25	0.98	0.76	0.75
O_I	0.284	0.25	0.687	0.88	1.00
O_{II}	−0.040	0.25	0.212	0.88	1.00

Coordinates taken from [5]. All atoms are in special positions 4*c* of space group *P*nma.

O_I and O_{II} were used for (Mg,Sn), O_I and O_{II} together with the same temperature factors, Table II. The Li^+ ions were excluded from the calculations since they would have a negligible effect on the intensities. The calculated and experimental powder data are given in Table III. Agreement between experimental and calculated intensities is reasonably good, especially since no attempt was made to improve the agreement by adjusting the atomic parameters.

There is considerable interest in $Li_2Ti_3O_7$ as a Li^+ ion conducting solid electrolyte [10]. Its conductivity is $\sim 10^{-7}$ to $10^{-6}\,\Omega^{-1}\,cm^{-1}$ at room temperature rising to $\sim 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at 300° C. Experiments are underway to measure the conductivity of $Li_2MgSn_3O_8$ and assess its possible usefulness as a solid electrolyte.

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TABLE III Experimental and calculated X-ray powder data for $Li_2MgSn_3O_8$.

d_{obs} (nm)	d_{calc} (nm)	hkl	I_{calc}	I_{obs}
0.501	0.500	200	6	4
0.457	0.455	101	100	71
0.3585	0.3575	201	2	4
0.2797	0.2793	301	48	47
0.2646	0.2656	011	1	52
	0.2641	210	34	
0.2570	0.2567	111	45	59
	0.2555	002	11	
0.2504	0.2502	400	11	14
0.2349	0.2346	211	7	10
	0.2275	202	2	
	0.2247	401	1	
0.2079	0.2078	311	11	13
	0.2028	302	2	
0.1948	0.1949	410	4	3
	0.1937	112	1	
	0.1864	501	1	
0.1838	0.1836	212	36	41
0.1787	0.1787	402	16	18
0.1698	0.1699	312	3	4
0.1675	0.1679	103	3	7
	0.1668	600	2	
	0.1612	203	1	
0.1598	0.1598	511	20	22
	0.1575	502	1	
0.1555	0.1555	020	7	10
	0.1550	412	2	
0.1517	0.1517	303	6	7
	0.1494	013	1	
0.1477	0.1477	113	11	25
	0.1471	121	6	
	0.1470	610	8	
0.1396	0.1397	602	2	2
0.1376	0.1377	701	5	4
0.1358	0.1363	313	2	10
	0.1358	321	8	
0.1328	0.1328	022	3	5
	0.1320	420	3	

Intensity data were scaled empirically by setting $\Sigma I_{obs} = \Sigma I_{calc}$. Experimental intensities were obtained from a diffractometer trace.

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*These authors assume that $LiFeSnO_4$ has the Ca_2SnO_4 structure, which is different to ramsdellite. The agreement between their observed and calculated X-ray intensities is rather poor and it seems more likely that their phase is, in fact, ramsdellite-like, as described in [5].